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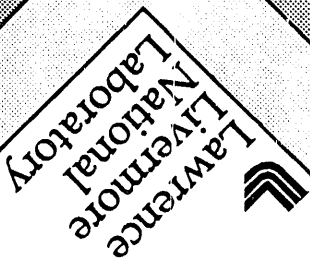
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32

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Pump-probe Method for Investigating Laser Ablation and Optical Damage
Threshold Mechanisms in Optical Materials

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I. Introduction

The interaction of intense laser beams with surfaces is of interest because of the importance of controlling and raising optical damage thresholds, and also because laser ablation is a useful process for surface machining, thin film deposition, and other applications. Despite several decades of research on the mechanisms of laser-surface interactions, the fundamental mechanisms of these interactions are in many cases poorly understood, particularly for materials that are nominally transparent at the laser wavelength. One reason for this lack of progress is that ablation very often occurs catastrophically in very small surface regions above a threshold laser fluence or intensity. Below the threshold, it has been difficult to obtain reliable information regarding the events leading up to ablation. The likely physical processes that are involved in ablation are linear and nonlinear absorption caused by bulk material near the surface, surface states, defects, and impurities. Recently, an experimental approach to probing these processes has been implemented, and some promising progress has been made in understanding optical damage mechanisms in several materials and optical coatings[1,2,3]. After a brief review of this work, some new insights that have been prompted by comparing the information obtained from these measurements with recent calculations of electron dynamics in solids in the presence of static and optical frequency electric fields will be discussed.

II. Pump-probe Method

Chase, et. al.[1] have developed a method for investigating laser-surface interactions by measuring the ratio of ablation threshold fluence for a pair of picosecond or subpicosecond laser pulses to the single-pulse ablation threshold. By varying the delay between the pulse pair, it can be determined if the laser-surface interaction is linear or nonlinear in the laser intensity and the lifetimes of the excitations (thermal, acoustic, electronic, etc.) that are produced by the interactions. In order to interpret this experiment it is assumed that the interaction of each laser pulse with the surface produces some excitation with amplitude p that is the primary cause of the surface damage. It is further assumed that p must exceed some threshold value p_t in order to cause ablation or optical damage. When two pulses are applied, the excitation produced by the second pulse adds to that remaining from the first pulse. Thus, even if neither of the pulses exceeds the damage threshold fluence, damage may still result from the pair of pulses. These assumptions may not be appropriate in all situations, for avalanche ionization processes, for example, but the model can be altered to account for other circumstances.

The simplest model that incorporates the above assumptions is based on two additional assumptions. First, it is assumed that the rate of energy absorption dE/dt from the laser beam depends only on the laser intensity, I , as a power law $dE/dt = KI^n$, where n is the order of the absorption process, and K is a constant. (In general, it is possible that k could vary during the laser pulses if there is accumulated surface modification cause by the laser beam.) Secondly, it is assumed that the excitation produced by the first pulse decays exponentially with a time constant τ_e . The excitation density $\rho(2, \tau)$ immediately after the second laser pulse can be written as

$$\rho(2, \tau) = c[F(2, \tau)/2]^n [1 + \exp(-\tau/\tau_e)] \quad (1),$$

where the first term is the excitation from the second pulse and second is that remaining from the first pulse. $F(2, \tau)/2$ is defined as the fluence of each of the identical laser pulses, and c is a constant proportional to K . The assumption of a unique threshold value, ρ_t , of the excitation density for optical damage to occur means that the value of the excitation should be the same at the damage threshold for a single pulse or for the pair of pulses, so $\rho_t(1) = cF_t(1)^n = \rho_t(2, \tau)$. Solving for the ratio of the double pulse and single pulse damage threshold fluences, $R(\tau) = F_t(2, \tau)/F_t(1)$, gives the experimentally useful result

$$R(\tau) = 2[1 + \exp(-\tau/\tau_e)]^{-1/n} \quad (2)$$

In general, a much more complicated expression for $R(\tau)$ might be applicable. Some possibilities are: cooling of a heated region due to thermal conduction or radiation; distributions of relaxation time for different surface regions or defects; distributions of threshold excitations or of values for the constant c . The details of the model are not as important as the basic idea of the experiment itself: assuming that the pulses are identical in intensity and fluence, the ratio of fluence to intensity is increased by a factor of two with two pulses as opposed to one pulse, with the added feature of a time delay. It is this feature that allows us to distinguish between linear and nonlinear absorption processes. Note that at small time delays $\tau \ll \tau_e$, the ratio $R(0)$ becomes $2^{(1-1/n)}$, from which n can be determined directly, independent of whether or not relaxation is exponential. On the other hand, at sufficiently long time delays, $\tau \gg \tau_e$, each pulse must independently exceed the damage threshold, which means that R will approach 2, regardless of the value of n . The time delay required for R to increase from its value at $\tau=0$ to its asymptotic value, $R=2$, gives at least a measure of τ_e , regardless of the specific details of the relaxation process.

III. Applications

This experiment has been performed on several types of bare and coated surfaces. The samples are mounted in a UHV chamber, and a quadrupole mass spectrometer is used as a detector of neutrals and ions ablated from the sample surface[1]. This provides a sensitive and immediate indication of when the ablation threshold is exceeded. In several materials, it is found that a multiple-pulse cumulative ablation mechanism occurs. This is referred to as "cumulative damage" and is commonly observed for optical damage of many optical materials and coatings which have substantially reduced optical damage threshold fluences when irradiated with more than one pulse at the same fluence. Figures 1 and 2 show the value of $R(\tau)$ for multiple pulse optical damage of single crystal (Wurtzite phase) ZnS and a common borosilicate glass, BK-7. Both samples were mechanically polished to obtain a good optical finish. These samples are chosen for illustration because much is known of their bulk optical properties at the dye laser wavelength, 580 nm used for the measurements. Each sample was exposed to a nominal 1000 pulses (or 1000 pulse pairs) to determine the multiple-pulse ablation threshold. It was found that the threshold changed negligibly for irradiation with more than 1000 pulses. The data for ZnS show unambiguously that, at small time delays, (yet large enough so that the pulses do not cause interference fringes on the sample) the ratio $R=1$, indicative of linear absorption as the basic mechanism for laser ablation. Values of R expected for nonlinear absorption due to multiphoton absorption and free-carrier heating ($R \sim 1.5$) are indicated on the figure for comparison. At time delays of several ns, R increases toward its expected asymptotic value of 2. The dashed curve shows a fit to Eq. 2 with $n=1$ and $\tau_e = 5$ ns. For BK-7, on the other hand, $R(0) \sim 1.7$, indicative of a very nonlinear laser-surface interaction. The large variability observed for R on different surface regions on BK-7 suggests that the surface condition is very important. The dashed curve in Fig. 2 is a fit to the data with $n = 5$ and $\tau_e = 2.2$ ns.

ZnS and BK-7 both have bandgaps that are substantially less than twice the photon energy used in these experiments, so two-photon absorption (TPA) is the lowest order intrinsic absorption process for the bulk material. The mechanism for optical damage for "pure bulk materials" often mentioned in the literature involves avalanche ionization initiated by the free carriers produced by multiphoton absorption [4]. In previous investigations, it has been very difficult to quantitatively explore the efficacy of this mechanism because of the lack of detailed knowledge of the physical properties of the media and of the interaction mechanism between the optical electric field and the free carriers. Recently, however,

Arnold and Cartier [5,6] have developed a quantum mechanical Monte-Carlo calculation method for treating the interaction of this field with free carriers in fused silica, which closely resembles BK-7 in many of its physical properties. Arnold and Cartier calculated the increase in energy of conduction electrons due to free-carrier absorption. They also calculated the impact ionization rate due to excitation of electron-hole pairs by the heated electrons. Impact ionization is the process in which an avalanche of ionized carrier density is produced by the laser field. This avalanche process is often regarded as the mechanism whereby energy is catastrophically deposited into the medium, resulting in optical damage.

Table I shows the bulk TPA coefficients, β , the measured single-pulse optical damage fluence, F_d , the maximum laser pulse intensity at the damage threshold, I_{max} , the free carrier density generated by TPA, n_{max} , the power absorbed per free carrier (from reference 6), the total deposited energy, E_{dep} due to two photon absorption (TPA) and free carrier absorption (FC), and the temperature increases ΔT due to these energy depositions for BK-7 and ZnS. It is assumed here that the free carrier heating rates calculated by Arnold and Cartier for SiO₂ are approximately correct for ZnS and BK-7 as well. This is probably not a bad assumption for BK-7, which approximates the structure and physical properties of silica except for the presence in BK-7 of modifier cations such as boron, but there is no justification other than necessity for assuming that these calculations offer reasonable approximations for ZnS.

Let us begin by considering ZnS. The TPA coefficient of this crystal is very large, typical of II-VI and III-V semiconductors at photon energies well above the TPA absorption edge [7]. At the peak intensities and fluences used for the data of Fig. 1 there is a very large free carrier density, $\sim 10^{20}$ cm⁻³ produced by TPA. Such a large carrier density is well above the values suggested for "seeding" of an electron avalanche, provided that the optical electric field is large enough and of sufficient duration for the avalanche to develop [4]. In fact, this carrier density is large enough that free carrier heating must be considered as a possible source of direct heating of the sample above its sublimation temperature. The estimated temperature rise due to free carrier absorption (~ 500 C) is indeed significant compared with the sublimation temperature of about 1100 C [8]. On the basis of these estimates, ZnS would seem to be a case where free carrier heating and/or electron avalanche is the most likely optical surface damage mechanism. Nevertheless, Fig. 1 shows that linear absorption is the cause of the cumulative optical damage mechanism. Linear absorption at a wavelength of 580 nm in ZnS could only be caused by impurities, color centers, or surface states. It is not possible to deposit sufficient energy into surface states to heat the sample locally to temperatures high enough to cause optical damage. A

reasonable conjecture, therefore, is that the linear absorption is caused by defect states, such as color centers, in the region near the surface. The cumulative, multiple-pulse nature of the optical damage implies that these defects grow in concentration on successive laser pulses until sufficient energy is deposited in a laser pulse to cause melting or avalanche breakdown of the surface region.

The two-photon absorption cross section for BK-7 at 580 nm is very small in comparison with that of ZnS. Although the optical damage threshold of BK-7 is about 2.5 times as large as that of ZnS, the energy deposited through direct TPA and free-carrier absorption is predicted in Table I to be negligible. The free carrier density due to TPA is nevertheless large enough that avalanche ionization could be the damage mechanism. The very nonlinear behavior implied by the data in Fig. 2 suggests this mechanism. For the laser pulse durations used in this work, the calculations of Arnold and Cartier imply that the laser intensity required for avalanche ionization to occur in bulk SiO₂ is considerably larger than the actual damage threshold field. If there are surface cracks or other sources of electric field enhancement in the surface region, however, it is possible that the local optical electric field at these defects is sufficient to cause avalanche ionization.

It is of interest to note that BK-7 is the only nominally transparent material investigated so far by this pump-probe method where nonlinear absorption processes were clearly indicated by the data as the cause of optical damage. This demonstrates that laser-surface interactions are often dominated by defect or impurity absorption, rather than intrinsic, multiphoton absorption.

IV. Conclusions

The pump probe experiment described here is a simple variant of a common experimental technique. It differs from the usual pump-probe measurement in the interpretation of the data because we are studying a phenomenon which requires a threshold intensity or fluence for its occurrence. This experiment essentially determines the relative influence of intensity and fluence of the optical field and the lifetimes of the excitations produced on the surface. The experimental results for ZnS and BK-7 glass demonstrate that intrinsic absorption mechanisms may not be significant indicators of optical damage mechanisms even when they lead to very high free-carrier densities and energy absorption.

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Table I

Parameters relevant to optical damage initiated by two-photon absorption and free carrier heating in ZnS and BK-7. The parameters, which are defined in the text, are appropriate for the 580 nm laser wavelength used for the data in Figures 1 and 2.

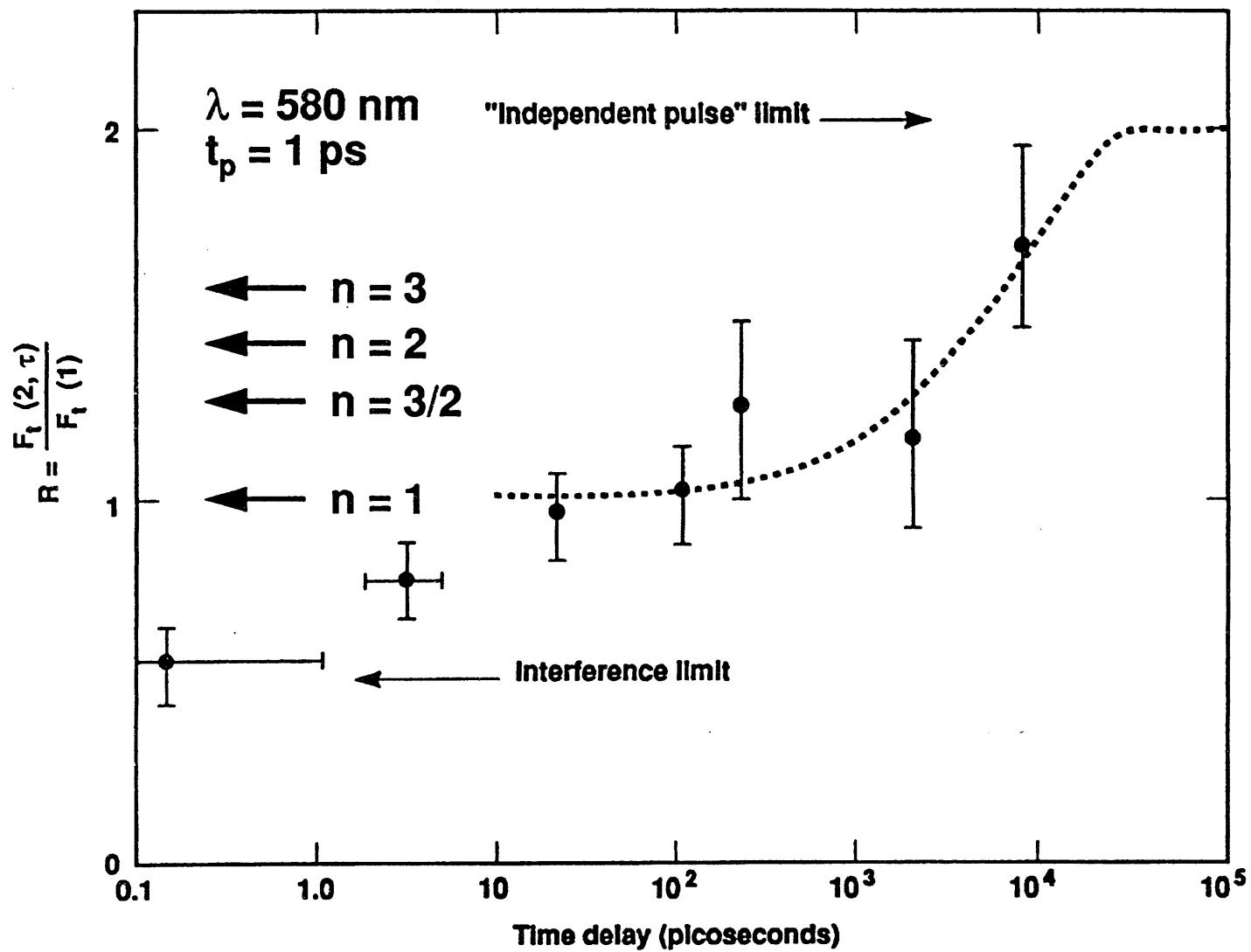
	ZnS	BK-7
β	2.3 cm/GW	~ 0.003 cm/GW
F_d	0.4 J/cm²	1.0 J/cm²
I_{max}	≥ 200 GW/cm²	≥ 500 GW/cm²
n_{max}	$\geq 10^{20}$ cm⁻³	$\geq 2 \times 10^{18}$ cm⁻³
$P_{abs}/carrier$	$\sim 3 \times 10^{-6}$ W	$\sim 5 \times 10^{-6}$ W
E_{dep} (TPA)	~ 100 J/cm³	~ 1 J/cm³
ΔT (TPA)	$\sim 100^\circ\text{C}$	$\sim 1^\circ\text{C}$
E_{dep} (FC)	~ 500 J/cm³	~ 10 J/cm³
ΔT (FC)	$\sim 500^\circ\text{C}$	$\sim 10^\circ\text{C}$

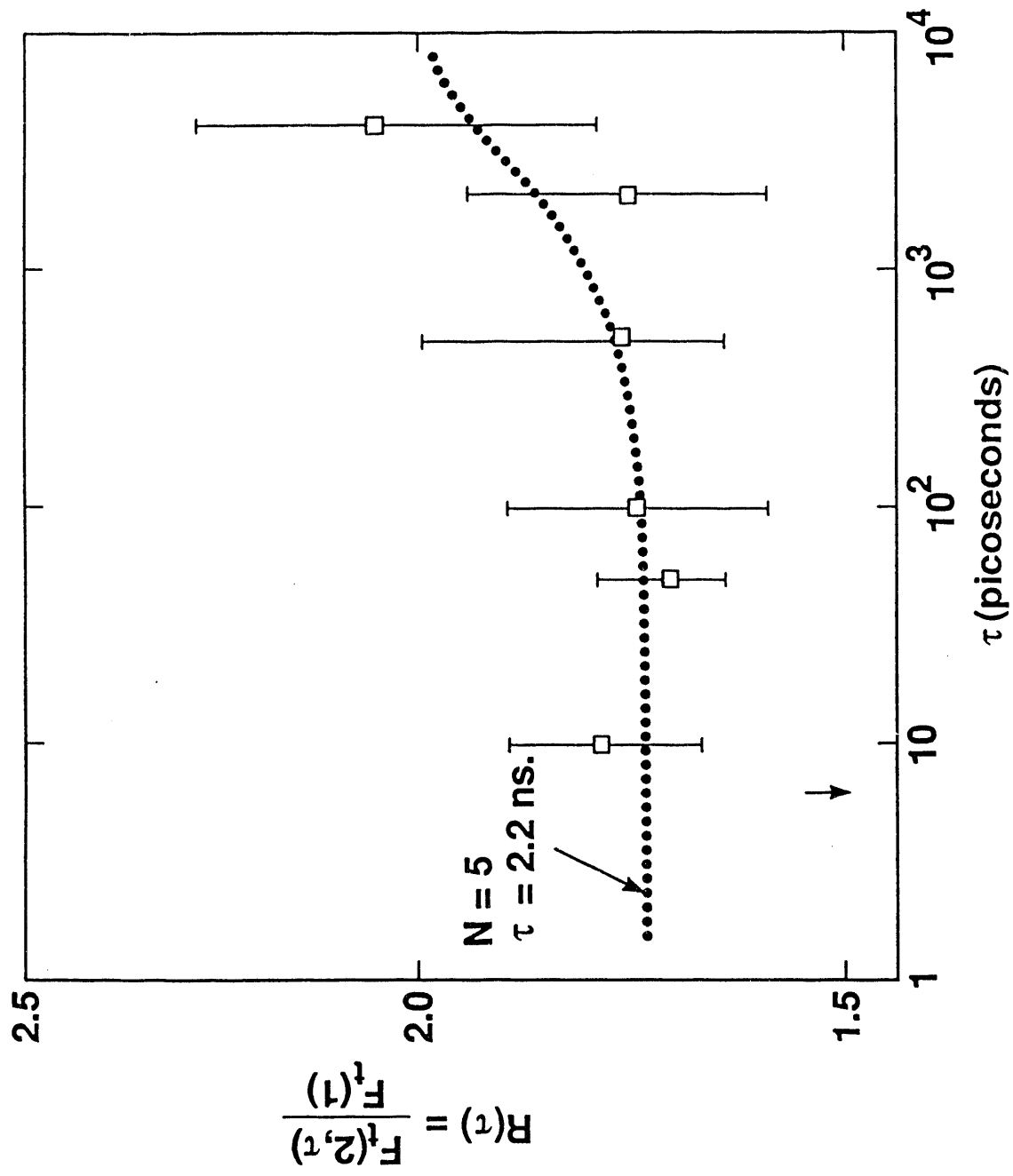
Figure Captions

Figure 1: Ratio of double-pulse cumulative optical damage threshold to the single-pulse threshold for ZnS versus time delay between the two pulses. The dashed curve is a fit to Eq. 2 with $n = 1$ and $\tau_e = 5$ ns.

The arrows at
left indicate the values of R at small time delays assuming
nonlinear absorption
of order n .

Figure 2: Ratio of double-pulse cumulative optical damage threshold to the single-pulse threshold for BK-7 glass versus the time delay between the two pulses. The dashed curve is a fit to Eq. 2 with $n = 5$ and $\tau_e = 2.2$ ns.





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